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in Aluminum Containers

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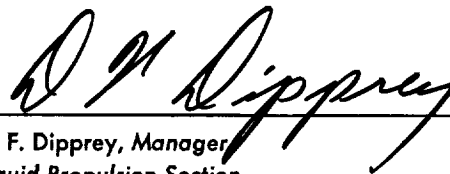
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A handwritten signature in dark ink, appearing to read "D F Dipprey", is written over a horizontal line.

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Liquid Propulsion Section

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

January 15, 1967

TECHNICAL REPORT 32-1039

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Contents

I. Introduction	1
II. Propellant Characteristics	2
III. Purpose of the Tests	3
IV. Storage Tests of Hydrazine and Nitrogen Tetroxide in Small Canisters of Type 2014 Aluminum Alloy	3
V. Storage Tests of Hydrazine in Small Canisters of Type 6061 Aluminum Alloy	7
VI. Storage Test of Hydrazine in a Flight-Weight Tank of Type 2014 Aluminum Alloy	10
VII. Firing Tests of Stored Hydrazine	17
VIII. Summary and Conclusions	18
Appendix. Cleaning Specification Tabular Data	21
References	21

Tables

1. Depth of corrosion in Vega fuel tank specimens	14
2. Hardness test results from Vega fuel tank specimens	16
3. Tensile test results from Vega fuel tank specimens	17
4. Summary of firing test data	17
A-1. Cleaning specification	21

Figures

1. Interior surfaces of canisters No. 1 and No. 2 (Type 2014 aluminum alloy) after 2-month storage of hydrazine	5
2. Canister M (Type 2014 aluminum alloy) after 2-month storage of hydrazine	6
3. Canister C (Type 2014 aluminum alloy) after 2-month storage of hydrazine	6
4. Canister No. 3 (Type 2014 aluminum alloy) after 2-month storage of nitrogen tetroxide	7

Contents (contd)

Figures (contd)

5. Canister No. 4 (Type 2014 aluminum alloy) after 1-month storage of nitrogen tetroxide	7
6. Typical canister storage test installation	8
7. Type 6061 aluminum alloy canister degreased and pickled, then used to store hydrazine 2 months	8
8. Type 6061 aluminum alloy canister which had been flushed with trichloroethylene, passivated 24 hours with hydrazine, then used to store hydrazine 2 months	9
9. Type 6061 aluminum alloy canister subjected to a "Liquid Hone" treatment, then used to store hydrazine for a period of months	9
10. Type 6061 aluminum alloy canister subjected to a "Chem Mill" treatment, then used to store hydrazine for a period of months	9
11. Section view of Vega fuel tank used for long-term storage test of hydrazine	11
12. Vega fuel tank during long-term storage test of hydrazine	12
13. Interior lower surface of Vega fuel tank after long-term hydrazine storage test and locations where metallographic samples No. 3 and No. 4 were taken	13
14. Interior mid-section surface of Vega fuel tank after long-term hydrazine storage test and locations where metallographic samples No. 2 and No. 7 were taken	14
15. Corrosion in Vega fuel tank specimen No. 4A, magnification $\times 500$	15
16. Corrosion in Vega fuel tank specimen No. 4B, magnification $\times 500$	15
17. Corrosion in Vega fuel tank specimen No. 6, magnification $\times 500$	15
18. Condition of outside surface of Vega fuel tank specimen No. 9, magnification $\times 500$	15
19. Corrosion in Vega fuel tank specimen No. 7, magnification $\times 500$	16
20. Condition of outside surface of Vega fuel tank specimen No. 7, magnification $\times 500$	16
21. Design of uncooled test rocket engine used to make comparison firings with stored and stock hydrazine fuel	18
22. Uncooled rocket engine on test stand at JPL's Edwards Test Station	19
23. Variation in theoretical shifting equilibrium c^* with addition of ammonia to hydrazine-base fuel burned with N_2O_4 at $r = 1.2$	20
24. Variation in theoretical shifting equilibrium c^* with addition of water to hydrazine when burned with N_2O_4 at $r = 1.2$	20

Abstract

Small canisters of Types 2014 and 6061 aluminum alloy were subjected to short-term compatibility tests with nitrogen tetroxide and hydrazine to determine the effect of different cleaning procedures. Only minor differences were noted. A flight-weight propellant tank of Type 2014 aluminum alloy was used to store hydrazine for 46 months. At the end of that test, the tank was found to be only slightly corroded. Firing tests showed the stored fuel delivered slightly less performance; but it ignited and burned as smoothly with nitrogen tetroxide as stock hydrazine burned with nitrogen tetroxide.

Storage Tests of Nitrogen Tetroxide and Hydrazine in Aluminum Containers

I. Introduction

The propellant storage tests described in this report were started as part of the Vega program. Vega was the first major effort undertaken by JPL for NASA. Formalized early in 1959, the program was aimed at launching several lunar and planetary spacecraft. A launch vehicle was planned which was to use a modified Atlas for the first stage; a second stage powered by a General Electric rocket engine and, when necessary, a new third stage to be developed by JPL.

The third stage incorporated a pressure-fed, bipropellant propulsion system rated at 6,000 pounds thrust. The system was built around an engine originally conceived as a device for demonstrating practicality of the earth-storable liquid propellant combination of nitrogen tetroxide and hydrazine for use in regeneratively-cooled thrust chambers. At JPL that propellant combination was considered the "successor" to the earth-storable combination of nitric acid and aniline. Sufficient experience had been accumulated by the Laboratory to utilize these propellants within the state of the art. The rocket industry at large, however, hesitated to exploit the advantages of these propellants because few companies had gone beyond research-type testing; during early tests some

difficulties had been experienced, particularly with hydrazine. One goal of 6K propulsion system development was to demonstrate the usefulness of these propellants in a flight program.

As in almost any flight vehicle, propellant tankage weight in the Vega third stage was critical. It was decided the tanks should be made of a high-strength aluminum alloy (Type 2014-T6). That posed the problem of assuring compatibility with propellants because, although the alloy had been in use for some time, definitive information on the degree of reaction with nitrogen tetroxide and hydrazine under actual storage conditions was not available.

The tests described in this report were initiated during the Vega program to provide empirical data on compatibility of propellants with Type 2014 aluminum alloy. Shortly after the work started, the Vega was cancelled; nevertheless, testing continued because of the general usefulness of the information to be obtained. Later, tests of Type 6061 aluminum alloy were added during the Mariner A program because of interest expressed in the more conservative material choice. Final phases of the full-sized tank storage test, hydrazine properties

analysis, and firing tests were supported as part of the Advanced Liquid Propulsion Systems (ALPS) program. The ALPS work, sponsored as an advanced development by the Office of Advanced Research and Technology, NASA, also aims at exploiting nitrogen tetroxide and hydrazine as propellants (Ref. 1).

II. Propellant Characteristics

The propellant combination of nitrogen tetroxide and hydrazine is easily handled, is storable at moderate temperatures, and has good performance. An important characteristic of the combination, which contributed to system reliability through simplification, was its hypergolic ignition—spontaneous ignition occurs within a few milliseconds of contact (Section VII).

Nitrogen tetroxide is an energetic oxidizer which exists in equilibrium with nitrogen dioxide ($\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2$). It is commercially available in large quantities at a purity of 99.5% or greater. The liquid boils at 70°F but its vapor pressure is low enough (48 psia at 120°F) to allow indefinite storage in light-weight sealed containers at moderate temperatures. The liquid is less than half as viscous as water.

The liquid burns the skin on contact (protective clothing must be worn when splashes or spills are possible) and the vapor is very toxic. Even concentrations which are invisible may exceed the maximum allowable concentration (MAC) for 8-hour exposure. Self-contained air supplies are required to provide positive protection from breathing the vapor. Water is the universal antidote for fires, spills, and skin contact. Usually, closed transfer systems are used to minimize the hazard to personnel and adjacent equipment.

Nitrogen tetroxide will not burn or thermally decompose at an explosive rate. It is a vigorous oxidizer which supports combustion. Although it is theoretically possible for nitrogen tetroxide to form shock sensitive compounds, there were no known cases of explosions or fires in test hardware due to reaction with contamination in any programs carried out by JPL that used this oxidizer. The degree of latent hazard seems substantially less than with oxygen. Nevertheless, considerable care is exercised to clean all surfaces in nitrogen tetroxide circuits. Cleaning processes for the several different system circuits (oxidizer, fuel, and gas) are sometimes standardized for the sake of convenience. Processes now used in flight hardware are similar to those commonly used for oxygen systems.

Dry nitrogen tetroxide is non-corrosive to many common metals; however, it is hygroscopic and reacts with water to form nitric acid which is very corrosive. Also, commercial nitrogen tetroxide often contains a small percentage of nitrosyl chloride (NOCl) which can attack many metals, including some usually considered quite corrosion resistant. Salts are frequently found on metal surfaces after the liquid has been drained off and the surface allowed to dry by evaporation over an extended period. Very few plastic materials are known which can resist attack by nitrogen tetroxide. The best elastomers available for nitrogen tetroxide service are severely degraded after 2 to 4 weeks' exposure; the recent development of nitroso terpolymer rubbers may provide the first known elastomer to be truly resistant to N_2O_4 .

Hydrazine is a strong reducing agent and has physical properties similar to water. It is commercially available in large quantities on special order. Purity of samples tested during the program averaged above 98.5%. Hydrazine is stored in drums for years and, when uncontaminated, it usually undergoes negligible changes in composition over these periods.

The liquid produces an alkali burn upon contact with skin, so protective clothing should be worn when spills or splashes are possible. It is extremely poisonous if ingested and the vapor is highly toxic, but the low vapor pressure of hydrazine makes accumulation of lethal concentrations unlikely wherever there is ventilation. Water is the best treatment for fires, spills, and skin contact. Usually, inert gas blankets and purges are used to displace air from hydrazine storage and transfer systems to minimize the possibility of reaction under conditions of adiabatic compression.

Although hydrazine is not shock sensitive, thermodynamic potential for explosive thermal decomposition has been one of the major deterrents to widespread use of neat hydrazine as a fuel. Work at JPL indicates that reliable utilization of hydrazine is dependent upon: (1) keeping it from contact with materials and types of surfaces that are actively catalytic or readily reducible, and (2) where heating is possible, eliminating zones of local flow stagnation and providing sufficient flow velocity for local conditions of bulk temperature and pressure, ensuring that the local value of heat flux at the upper limit of nucleate boiling safely exceeds local heat flux. From the first statement comes the requirement to avoid metallic oxides—the most prevalent cause of accelerated hydrazine decomposition. Cleaning and operational procedures must remove oxides and prohibit their

formation. Aluminum oxide seems to be an exception to the rule and is considered compatible with hydrazine.

Hydrazine affects many metals and the degree of reaction apparently is dependent upon the surface treatment. For example, cleaning procedures used for the metal canisters (discussed in Section IV) affected the amount of copper leached from the aluminum alloy. Dilute hydrazine may be more reactive than the pure substance. During the Vega program the fuel circuit in the heavy-weight feed system (used for static test firings) was flushed with distilled water and drained after many of the tests. The bottom flange on the fuel tank and the fuel flowmeter case were made of aluminum alloy. Periodic examination revealed pitting and formation of aluminum hydroxide. The corrosion was attributed to dilute hydrazine film remaining on the surface after the tank was flushed and drained. Hydrazine also attacks some plastics and elastomers but materials of that type, which have excellent resistance, are available. Hydrazine dissolves most surface coatings and adhesives.

From the foregoing general descriptions, it is apparent that nitrogen tetroxide and hydrazine create certain storage problems; these problems are not as severe as might be supposed by the uninitiated, however, if judged relative to behavior of other common earth-storable propellants. Dry nitrogen tetroxide is much more passive to metals than red or white fuming nitric acid. Cleanliness is far less critical with it than with hydrogen peroxide. Hydrazine, while it attacks metals more vigorously, is compatible with many more plastics and elastomers than is unsymmetrical dimethylhydrazine.

III. Purpose of the Tests

At the time the storage test program was started, most of the available compatibility information about these propellants was obtained in chemistry laboratories by immersing coupons, slabs or O-rings into beaker-sized volumes of propellant¹. Otherwise, such data were in the nature of vague generalities based on test pit experience where propellants had been kept for short periods in ASME-type vessels of stainless steel. Almost all of the long-term storage data were derived from experience with the suppliers' shipping containers.

¹A new method of making compatibility tests using small materials samples has recently been developed as part of the ALPS program. The work will be reported in JPL Technical Reports.

It remained, therefore, to develop more definitive information on how well nitrogen tetroxide and hydrazine could be stored for long periods in the particular light-weight alloys of interest for flight tankage. Furthermore, it was important to learn how compatible were the propellants and actual tankage structures that had weld beads and joints. Compatibility, in this context, means both the effect of propellants on tanks and vice versa. Weakening of the tanks through corrosion was obviously detrimental, as was decomposition of propellants in contact with the tanks. Such decomposition would increase pressure in the tanks and raise the temperature of the tanks and propellants. It could also affect combustion characteristics of the propellant combination.

Because complex and unpredictable interactions between tanks and propellants were expected, the test program was slanted toward generating empirical data under conditions that to some degree duplicated those a flight tankage system might experience. The goal was to actually measure pressure rise in containers filled with propellants as a function of surface treatment given the containers. Also, qualitative information was to be developed on the corrosion of containers by post-test examinations. Late in the program, it was decided that some indication of effect of long-term storage on combustion characteristics of hydrazine should be obtained.

IV. Storage Tests of Hydrazine and Nitrogen Tetroxide in Small Canisters of Type 2014 Aluminum Alloy

At the beginning of the program it was decided that it was not feasible to do all testing with full-sized Vega tanks because of the limited number of tanks available and the magnitude of such an undertaking. Instead, a plan was formulated that included a preliminary phase devoted to screening the several alternate surface cleaning and treatment procedures to discover which method resulted in least tank corrosion and propellant decomposition. These screening tests were to be accomplished with a number of small test canisters constructed of the same material as the Vega tanks.

Two canisters, designated No. 1 and No. 2, were fabricated of Type 2014-T6 aluminum alloy tubing and plate for testing with hydrazine (N_2H_4). These cylindrical canisters had an internal diameter of approximately 7.4 inches. Both were welded with a manually-operated "Heliarc" welder using a rod of 43S aluminum containing

5% silicon. No attempt was made to keep an inert atmosphere inside the canisters during welding. Canister No. 1 was cleaned by first rinsing with trichloroethylene, then washing thoroughly with a commercial aviation-type detergent, rinsing with distilled water, pickling with an acid solution, rinsing again with distilled water, and finally drying with nitrogen gas. Canister No. 2 was cleaned with trichloroethylene, rinsed with distilled water, and dried with nitrogen gas. The volumes of the canisters were measured to an accuracy of $\pm 0.5\%$ and found to be 3600 milliliters for No. 1 and 3582 milliliters for No. 2. The canisters were then hydrostatically proof-tested to 25 psig with distilled water and dried again with nitrogen gas.

Bourdon-type pressure gauges of Type 316 stainless steel alloy and immersion-type thermometers of 18-8 stainless steel were installed to measure the pressure and temperature of the contents of the canisters. Fittings on the canisters were made of either Type 303 or 347 stainless steel. Teflon O-rings were used as seals and the pipe threads were wrapped with teflon tape. An explosively-actuated valve was attached to each canister so they could be remotely vented in an emergency. The valves were constructed of Type 17-4 PH stainless steel and Type 2024-ST aluminum alloy. All of these appurtenances to the canisters were cleaned with trichloroethylene, rinsed with distilled water and dried with nitrogen before assembly into the canisters. The entire assembly was leak tested with nitrogen gas at 25 psig—no leaks were found.

Canister No. 1 was filled with 3466 milliliters and No. 2 was filled with 3448 milliliters of hydrazine. The hydrazine was chosen from batches that analyzed 99.5 to 99.7% N_2H_4 and less than 0.1% NH_3 (ammonia). Both canisters were stored in the shade for 1 month and then in direct sunlight for 1 month at JPL's Edwards Test Station; during this 2-month period the canisters were kept in a horizontal position. Readings of the canister pressure, liquid temperature and ambient temperature were taken every hour for the first 8 hours, then three times during each working day for 2 months.

During the 2-month test period, the recorded ambient temperature ranged from $+29$ to $+94^\circ F$; the higher temperatures occurred during the first 2 weeks of the test, the lower temperatures during the last 2 weeks. In canister No. 1, liquid temperatures ranging from $+23$ to $+87^\circ F$ were noted, while in canister No. 2 the temperatures read were $+22$ to $+91^\circ F$. Discrepancies between extremes of recorded ambient and liquid temperatures

were probably due to instrumentation errors and actual lags between changes in ambient and liquid temperatures due to the slow rate of heat transfer between the atmosphere and the liquid. Measured pressures ranged from 0 to $+7$ psig in canister No. 1 and 0 to $+6\frac{3}{4}$ psig in canister No. 2.

The meaning of temperature-pressure data was very difficult to assess because of inherent lack of accuracy in the instruments used to gather data, the possibility of leakage from containers, and lack of good data on solubility of decomposition products of hydrazine in liquid hydrazine.² However, an attempt was made to gain a feeling for the "relative" compatibility of the containers in terms of the amount of undissolved gas accumulated over the liquid. It was assumed that the decomposition products obeyed the ideal gas law and that at a given liquid temperature, the degree of solubility was a constant, regardless of pressure. Then from the canister volume, liquid volume, and the temperature, a calculation was made of the weight of gas over the liquid as a function of test time. A plot was made of all the data points for liquid temperatures between $+60$ and $+65^\circ F$. The results of these calculations showed an increase of approximately 1.6×10^{-6} pounds per day of decomposition products in both canisters. (Approximately 1160 square centimeters of interface existed between the liquid and metal in canister No. 1 and 1150 square centimeters in canister No. 2.) It should be noted that because of constantly changing liquid temperature, this rate of decomposition is an integrated summation reduced to a reference temperature range (60 to $65^\circ F$), and not necessarily the rate at the reference temperature. At completion of the test, all the liquid was decanted. Hydrazine from canister No. 1 contained finely divided sediment. The analysis was 99.3% N_2H_4 , 0.1% NH_3 , less than 0.001% non-volatile matter, and a residue which was more than 50% copper (the remainder being aluminum). Hydrazine from canister No. 2 appeared to have gray, fluffy matter in it. The analysis was the same as from canister No. 1, except that the residue was 6% copper and 94% aluminum. After sectioning, canister No. 1 appeared to be fairly clean inside, while No. 2 was somewhat more discolored and corroded. Figure 1 shows the internal appearance of the two canisters.

Two more canisters, labeled M and C, were fabricated as before. Canister M was not cleaned, except for being

²The data of Thomas (Ref. 2) indicate an ammonia concentration of approximately 0.3 mole % would be necessary to give rise to a pressure increase (at $+100^\circ F$) detectable in the experiments described in this report.

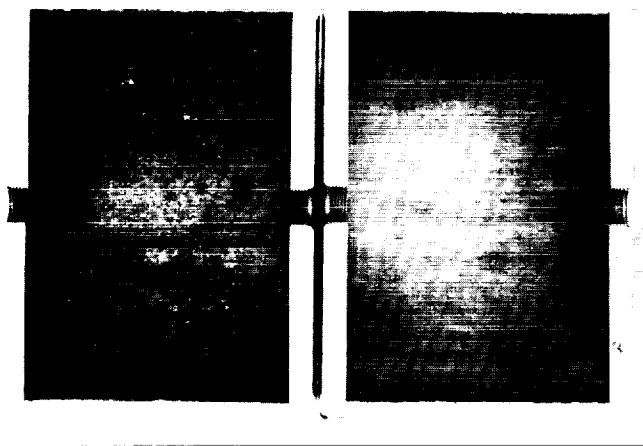


Fig. 1. Interior surfaces of canisters No. 1 and No. 2 (Type 2014 aluminum alloy) after 2-month storage of hydrazine

wiped with a rag soaked in acetone to remove oil and grease prior to welding and wire brushing on the surfaces to be welded. Cleaning was avoided so that the compatibility of the "mill surface", as received, could be determined. The parts for canister C were cleaned by sanding the entire inner surface to a 125-micro-inch finish, then degreasing and "chem milling" approximately 0.0005 inches from the stock, using a mild base solution. The edges were not wire-brushed prior to welding. The procedure was the same as proposed for cleaning Vega propellant tank parts. The volumes of the canisters were measured to an accuracy of 0.5% and found to be 5600 milliliters for canister M and 5725 milliliters for canister C. Canisters were then hydrostatically proof-tested to 100 psig with distilled water and dried with nitrogen gas. The canisters were then fitted with the gauges and valves, as were canisters No. 1 and No. 2 previously described.

Canister M was filled with 5376 milliliters of hydrazine; canister C, with 5496 milliliters. A sample of hydrazine from the same drum analyzed as 98.3% N_2H_4 and 0.5% aniline. The canisters were stored in shade for 1 month and then in direct sunlight for 1 month at Edwards Test Station. As with canisters No. 1 and No. 2, these canisters were kept in a horizontal position. Readings of canister pressure, liquid temperature, and ambient temperature were taken three times each working day.

Ambient temperatures recorded during the test period varied from +43 to +108°F. Moderate temperatures prevailed during the early part of the test, then extremes

of hot and cold occurred during the latter two-thirds of the period. In canister M the records show liquid temperatures ranged from +37 to +108°F, while the temperatures in C varied from +35 to +107°F. Measured pressures in both canisters reached +13 psig.

Plots of data, calculated in the same manner as for canisters No. 1 and No. 2, showed increases in gas weight for the first 30 days, then no further evolution of gas. The rate was the same as for canisters No. 1 and No. 2. At completion of the test, all the liquid was decanted. It appeared normal with no visible sediment. Analysis of hydrazine from canister M was 99.2% N_2H_4 , 0.5% aniline, and less than 0.0001% non-volatile matter. Analysis of hydrazine from canister C gave the same results, except the N_2H_4 content was 99.0%. Little scale was found in either canister but canister M appeared more discolored. Figures 2 and 3 show these canisters after sectioning.

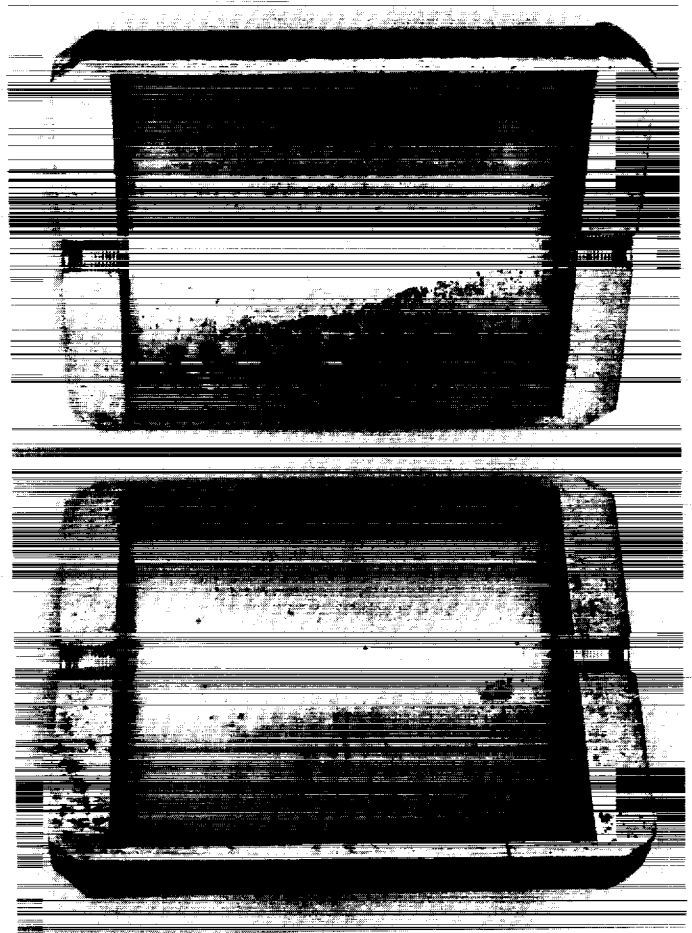
It was concluded from the canister tests that rate of hydrazine decomposition was relatively unaffected by any of the cleaning procedures. The ability of the 2014 aluminum alloy to withstand hydrazine attack was somewhat dependent upon surface treatment.

Two canisters, designated No. 3 and No. 4, were fabricated of 2014-T6 aluminum tubing and plate for testing with nitrogen tetroxide. The fabrication technique was the same as employed for hydrazine canisters No. 1 and No. 2 previously described. Canisters were cleaned by first rinsing them with trichloroethylene, then washing thoroughly with a commercial aviation-type detergent, rinsing with distilled water, and finally drying with nitrogen gas. In addition to being cleaned, canister No. 4 was "passivated" by keeping it full of nitrogen tetroxide for 24 hours. The volumes of canisters were measured to an accuracy of $\pm 0.5\%$ and found to be 4240 milliliters for No. 3 and 4297 milliliters for No. 4. Canisters were then hydrostatically proof-tested with distilled water to 120 psig and then dried. They were fitted with gauges and valves, as were canisters No. 1 and No. 2. Canister No. 3 was filled with 4070 milliliters and No. 4 was filled with 4125 milliliters of nitrogen tetroxide and were placed on their sides in shade at Edwards Test Station. Readings of canister pressure, liquid temperature and ambient temperature were taken as for canisters No. 1 and No. 2.

No indication of reaction was observed on the instruments. (A slight rise in pressure was noted as ambient temperature warmed during each day, attributed to normal increase in vapor pressure of the nitrogen tetroxide.)



**Fig. 2. Canister M (Type 2014 aluminum alloy)
after 2-month storage of hydrazine**



**Fig. 3. Canister C (Type 2014 aluminum alloy)
after 2-month storage of hydrazine**

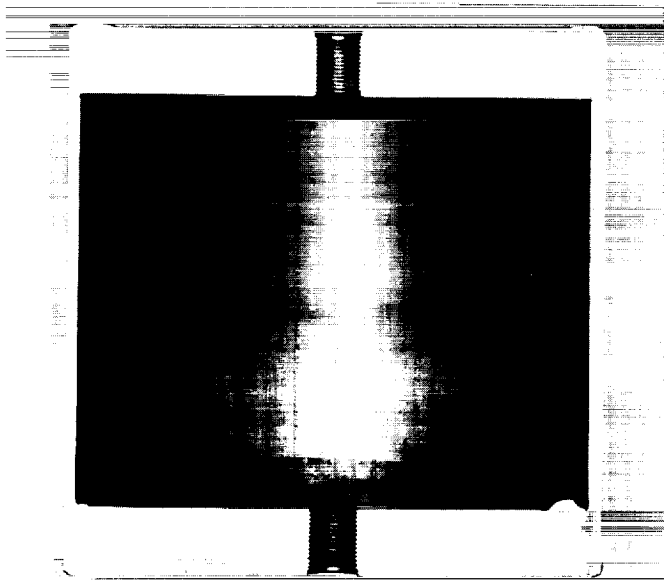


Fig. 4. Canister No. 3 (Type 2014 aluminum alloy) after 2-month storage of nitrogen tetroxide

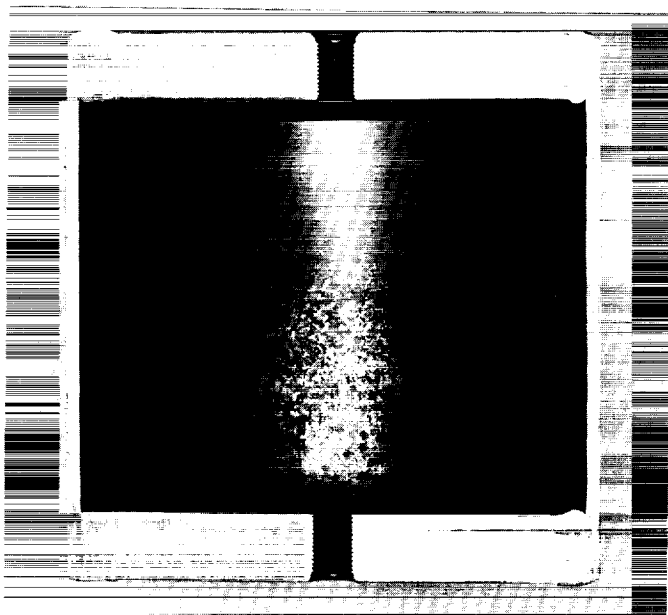


Fig. 5. Canister No. 4 (Type 2014 aluminum alloy) after 1-month storage of nitrogen tetroxide

At completion of the test, all the liquid was decanted. It appeared normal with no visible sediment. Analysis showed the composition of the nitrogen tetroxide to be virtually unchanged; there was 0.1 to 0.2% water, and 0.0001% Fe_2O_3 which probably came from the shipping

container before the test started. The canisters were sectioned for examination. A multitude of small pits were found on the interior surfaces. These pits were between 0.0001 and 0.0002 inches deep. Canister No. 4 was somewhat more discolored than No. 3; the reason for that was not discovered. Figures 4 and 5 show the internal appearance of the canisters after test. It was concluded from these tests that 2014-T6 aluminum, cleaned according to the procedure used, is suitable for storage of nitrogen tetroxide and that the 24-hour "passivation" was unnecessary.

V. Storage Tests of Hydrazine in Small Canisters of Type 6061 Aluminum Alloy

Eight small canisters were fabricated of 6061-T6 aluminum tubing and plate. As before, a hand-operated Heliarc welder and 43S aluminum alloy rod were used without any inert atmosphere inside the container. Final machining was done after heat treating the assembly to the T6 condition. All the finished canisters had internal dimensions of approximately 5.0 inches in diameter and 7.9 inches in length, giving an average internal volume of 2540 milliliters. Canisters 1 and 5 were cleaned by rinsing with trichloroethylene, drying, pickling with a solution of nitric and hydrofluoric acid for 5 minutes, rinsing with distilled water, and finally drying with nitrogen gas. Canisters 2 and 6 were cleaned by rinsing with Furfisol M-17 solvent (manufacturer: John B. Moore Corporation, Nutly, New Jersey), then passivating with anhydrous hydrazine which was drained out after approximately 24 hours. Canisters 3 and 7 were prepared by a commercial firm which had subjected the interior surfaces to a "liquid honing" process. Interiors of canisters 4 and 8 were given a "chem milling" treatment by a commercial company. All the canisters were hydrostatically proof-tested to 400 psig with distilled water and then dried with nitrogen gas.

Instrumentation similar to that used for the previous tests (described in Section IV) was installed on each canister. Instead of the explosively-actuated valves, however, every canister was fitted with a burst-disc assembly for protection against excessive pressure build-up. Each of the canisters was loaded with 2134 milliliters of anhydrous hydrazine. All eight canisters were then placed in a vertical orientation in shade at JPL's Edwards Test Station facility. Figure 6 shows four of the canisters in the storage shed. Readings of canister pressure, liquid temperature, and ambient temperature were taken twice each working day for 2 months. Recorded

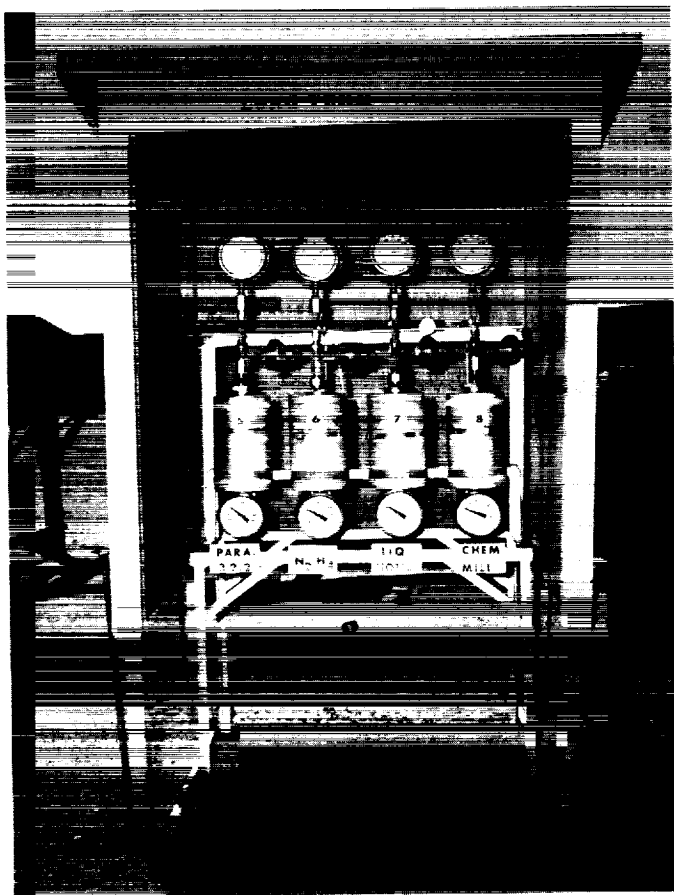


Fig. 6. Typical canister storage test installation

ambient temperatures ranged from +53 to +112°F during the test period, the higher temperatures occurring toward the end of the test.

During test period, temperatures recorded for the liquid in canister No. 1 varied from a low +37°F to a high +97°F. Maximum pressure recorded during that period was 1 psig. No trend of hydrazine decomposition could be inferred from such meager data. When the canister was cut open, its interior was found free of scale and there was no noticeable discoloration or pitting (Fig. 7).

The recorded temperatures for the liquid in canister No. 5 ranged from +42°F to +98°F during the same period, while the pressure was varying from 0 to 5 psig. Since this canister received the same treatment as No. 1, the substantial difference in pressure is noteworthy. No specific explanation for the difference was discovered, but the data show higher pressures from the start of the test, which might infer a pressure leak in No. 1, but

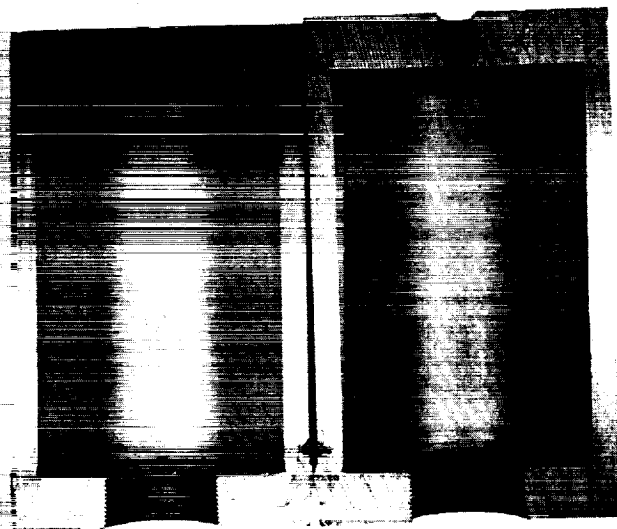


Fig. 7. Type 6061 aluminum alloy canister degreased and pickled, then used to store hydrazine 2 months

No. 5 was leak-tight. Plots of points calculated from data taken at liquid temperatures between +80 and +90°F show an accumulation of 3.8×10^{-6} pounds per day for the first 30 days, then a drop in rate to 1.2×10^{-6} pounds per day. The liquid-to-metal interface was 806 square centimeters.

Canister No. 2 registered pressures ranging from 0 to 6½ psig, and the recorded liquid temperatures were all between +39°F and +99°F. The plots of data indicated about the same gas evolution trend as for canister No. 5. While the interior of this canister showed no scaling or pitting, there were patches of dark discoloration; such patches are not particularly visible in the photograph (Fig. 8).

Liquid temperatures of from +45°F to +102°F were recorded for canister No. 6, but the pressure gauge always read zero psig. In that case, also, it seemed unlikely that two canisters, treated exactly alike, would differ so much in pressure build-up. The zero pressure reading, regardless of temperature, made that data suspect and raised doubts about leak-tightness of the assembly.

Recorded liquid temperatures were from +37°F to +98°F in canister No. 3. The recorded pressures were 0 to 1 psig. A slight amount of dark discoloration was observed when the canister was sectioned, but there was no visible scaling or pitting (Fig. 9).

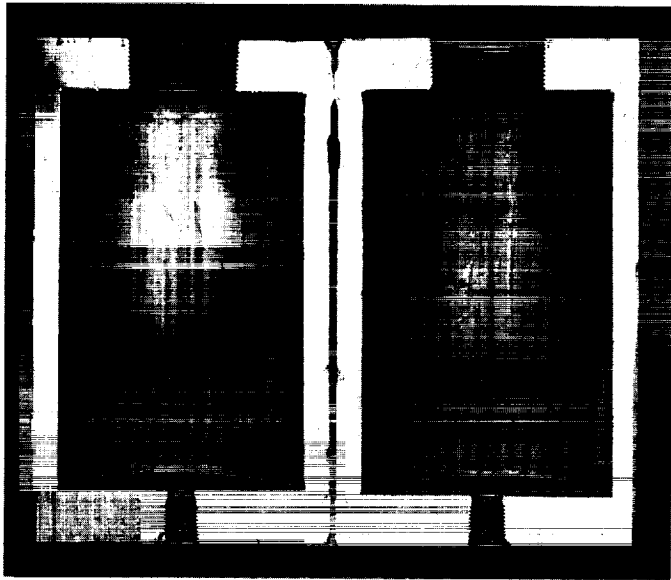


Fig. 8. Type 6061 aluminum alloy canister which had been flushed with trichloroethylene, passivated 24 hours with hydrazine, then used to store hydrazine 2 months

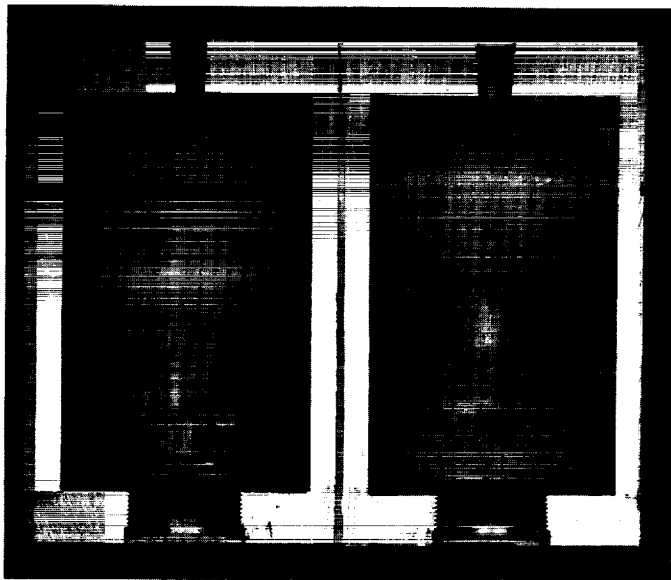


Fig. 9. Type 6061 aluminum alloy canister subjected to a "Chem Mill" treatment, then used to store hydrazine for a period of months

Canister No. 7 instruments indicated a temperature range of $+44^{\circ}\text{F}$ to $+101^{\circ}\text{F}$ and a pressure variation of 0 to 5 psig. That canister and No. 3 were given the same processing so the discrepancy in pressure readings raised doubts about leak-tightness of No. 3. Scatter in the data

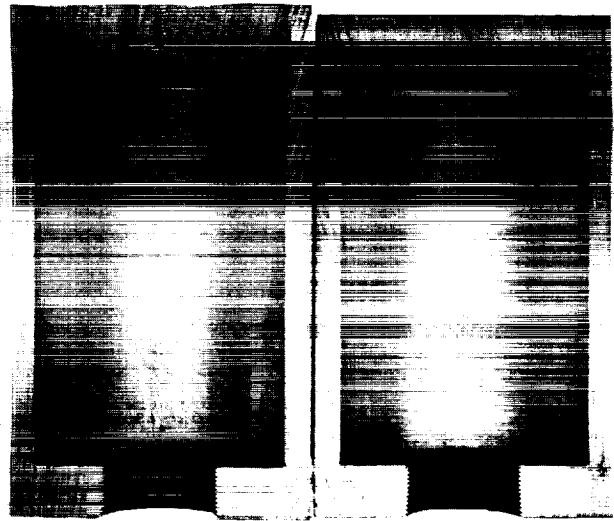


Fig. 10. Type 6061 aluminum alloy canister subjected to a "Liquid Hone" treatment, then used to store hydrazine for a period of months

for No. 7, however, made evaluation of decomposition rate impossible.

For canister No. 4, the recorded temperature extremes were $+30^{\circ}\text{F}$ and $+90^{\circ}\text{F}$ and the data show only zero gauge pressure. Inside surfaces were very clean and free of scale or discoloration; no pitting from corrosion was visible but the surface was rough, as is typical of chemically-milled surfaces (Fig. 10).

The other chem-milled canister, No. 8, also gave zero pressure readings. Liquid temperatures of $+38^{\circ}\text{F}$ to $+95^{\circ}\text{F}$ were recorded.

Post-test analysis of hydrazine showed no measurable change in basic composition. Samples from canisters 1 through 4 were 99.3 to 99.4% hydrazine and 0.5% aniline. Non-volatile residue (as Fe_2O_3) was about 0.001% in canisters 1, 3, and 5, and 0.003% in canister 2.

The exact degree of hydrazine decomposition was not determined. Such a determination would involve pre-test and post-test analysis for water, ammonia, nitrogen and hydrogen. To do that would have required the hydrazine to be transferred under pressure into the sampling vessels so that the dissolved products of the decomposition (ammonia, nitrogen, and hydrogen gases) would not effervesce and be lost. The validity of conclusions drawn from this more complete analysis would still be open to

question because of the possibility that leakage occurred during the test and allowed some of the gaseous products to escape.

In addition to the questions about the leak-tightness of these assemblies, there was some doubt about the accuracy of temperature data. Only small differences in temperature would ordinarily be expected, since the canisters were mounted side-by-side in two installations (Fig. 6). The data show differences as great as 12°F between readings taken at any one time. The thermometers on canisters 1, 3, and 5 usually read within 2 degrees of each other, while that on canister 2 averaged 2 degrees higher. Randomly higher readings were obtained from canisters 6 and 7; these read as much as 12°F greater than 1, 3, 5, and 2. Readings averaging 4°F lower were gotten from canister 8, and the thermometer on canister 4 usually read 8 to 12°F lower than 1, 3, and 5.

Despite the problems of interpreting data, the tests did seem to indicate that Type 6061-T6 aluminum alloy was not seriously affected. With the degreased-pickled samples and the chem-milled samples, there was no appreciable degree of discoloration.

VI. Storage Test of Hydrazine in a Flight-Weight Tank of Type 2014 Aluminum Alloy

Upon completion of the screening tests, using small canisters, the full-size Vega propellant tank was prepared for a long-term storage test with anhydrous hydrazine. The tank was nearly spherical in shape except for the very bottom, which had a truncated cone. Overall, it was 62.66 inches high and 56.2 inches in diameter at the "equator." The internal volume was approximately 55.5 cubic feet. It was designed for a working pressure of 250 psia and a burst pressure of 325 psia at +120°F. Minimum wall thickness was 0.036 inch. But in many areas, substantially thicker sections were necessary, as in the transition sections, near weld seams, and wherever bending loads would exist—such as at the mounting lugs. Two anti-slosh baffle rings were installed inside the tank. Figure 11 shows the construction of the tank.

Lockheed Aircraft Company of Burbank, Calif., fabricated the tank of Type 2014 aluminum alloy. The main sections were spun from flat sheet, and bosses at top and bottom were machined from thick plate stock. Inert-gas-shielded arc welding was used to make all seams. Except

for grinding some of the weld beads, none of the surfaces received any special treatment (e.g., anodizing), but were left in the "as machined" condition.

The tank was cleaned by first rinsing with trichloroethylene, then thoroughly washed with a commercial aviation-type detergent, rinsed with distilled water, pickled with an acid solution, washed again with detergent, rinsed with distilled water, and dried with warm nitrogen gas. (Cleaning procedure described in detail in Appendix.)

Upon receipt at JPL, the tank was proof-tested and fitted with the necessary appurtenances for the test. These included a bourdon-type pressure gauge and two vent valves connected to the top port of the tank, a standpipe running from one of four bottom ports up to the middle of the tank (for securing propellant samples from the center of the propellant bulk), a dial thermometer inserted through another of the bottom ports, and two drain valves, plus miscellaneous necessary fittings attached to the bottom ports. All of these articles were constructed of aluminum, stainless steel, and/or Teflon. All seals were Teflon. Each of these parts was carefully cleaned before installation.

The tank assembly was mounted in a special frame and placed in direct sunlight at JPL's Edwards Test Station (Fig. 12). On July 27, 1960, after having been leak tested to 25 psig with nitrogen gas, it was filled with approximately 2580 pounds of anhydrous hydrazine. The ullage, about 14.5 cubic feet, was pressurized to 5 psig with nitrogen gas.

Samples were taken from the six drums of hydrazine used to fill the tank; the weighted average of the six analyses (using a method estimated to be accurate within $\pm 0.5\%$ hydrazine) showed these consisted of 98.1% hydrazine, 0.7% aniline, and less than 0.0001% insoluble matter by weight. Periodically, samples of hydrazine were withdrawn from the center (using the standpipe) and from the bottom of the tank. This was done approximately once every 2 weeks for the first year, once every month during the following 6 months, then once each 6 months for the remainder of the test. These samples were analyzed for hydrazine, aniline, and insolubles. Neither water nor ammonia was checked; analysis for ammonia would have been meaningless anyway, unless very special precautions were taken to avoid loss of ammonia during the process of drawing and transporting samples.

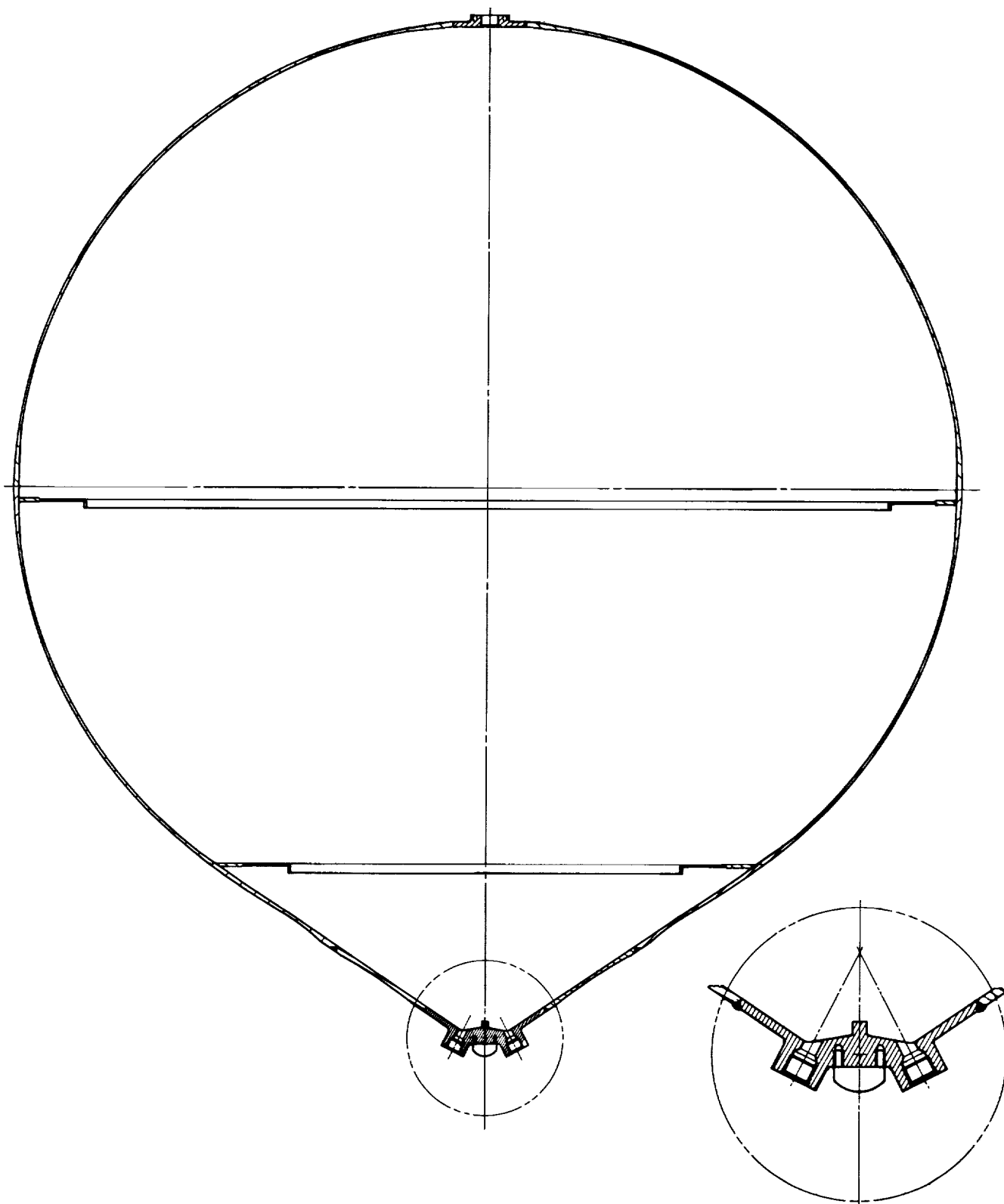


Fig. 11. Section view of Vega fuel tank used for long-term storage test of hydrazine

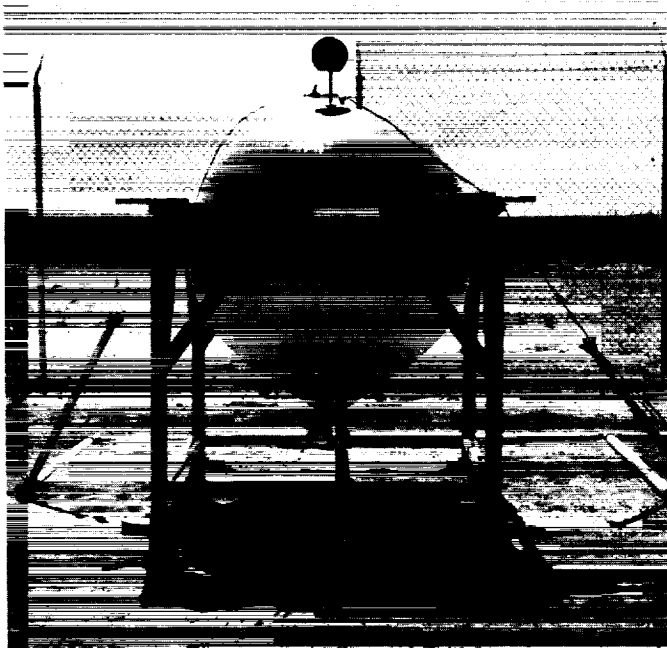


Fig. 12. Vega fuel tank during long-term storage test of hydrazine

The first samples, taken from the tank on August 8, 1960, contained a very small amount of black residue analyzing high in aluminum, iron, and copper. Subsequent samples were clear with no noticeable solid matter. In some cases there was just enough metal content to be detectable with the analytical procedures used. All analyses made during the first 3 years indicated a concentration of $98.6 \pm 0.6\%$ hydrazine and $0.5 \pm 0.1\%$ aniline by weight; non-volatile solids never exceeded 0.002%. The last two analyses, taken in January and May, 1964, showed 97.0 and 96.5% hydrazine, respectively; no explanation for this decline in hydrazine concentration after $3\frac{1}{2}$ years is known for certain. Perhaps slight variations in sample handling altered the amount of dissolved ammonia retained in the samples.

The chronological history of the hydrazine composition is somewhat obscured by lack of data on ammonia and water content. It is felt, however, that a considerable amount of dissolved ammonia (a decomposition product of hydrazine) was present in the hydrazine, toward the end of the test.

Taken at face value, the data do not reveal any measurable build-up in vapor pressure over the liquid during the 26 months data were gathered. That is to say, at any given temperature, the tank pressure was the same (within the apparent accuracy of instrumentation) at any time

during the test period. That tended to indicate the rate of hydrazine decomposition was very slow and that a sufficient volume of hydrazine was available in which the decomposition products could be dissolved and leave only a negligible amount of these products in the ullage. Of course, the possibility of gas leaks cannot be completely ignored, but positive pressures of the order of 2 to 5 psig were indicated to exist continuously over periods of several months during each warm season.

On May 6, 1964, the hydrazine was drained from the tank. Using methods accurate to $\pm 0.5\%$ hydrazine, measurements were made of the composition of samples taken from the six drums, into which all but the first and last quantities were drained. Three samples analyzed 96.2% and three samples analyzed 96.4% hydrazine; the average of 96.3% compared favorably with the final analysis of 96.5% for the final sample taken from the tank before draining. The seventh drum, containing a few pounds of the "worst" hydrazine (i.e., the first and last quantities), yielded a sample that was 95.6% hydrazine.

Another sample from the seventh drum and a sample of ordinary hydrazine from JPL's regular stock were obtained later during a series of firing tests (described in Section VII). These two samples were sent to an independent laboratory³ for comparative analysis, measurement of physical properties, and tests of ignition lag with nitrogen tetroxide (N_2O_4). The stored material was found to be approximately 97.84% N_2H_4 , 0.45% aniline, 1.86% water, and 0.01% insolubles. No explanation was available for the discrepancy between that analysis and the several made on similar samples by JPL. The stock hydrazine was 98.62% N_2H_4 , 0.23% aniline, 1.28% water, and 0.01% insolubles; that was believed to be very close to the original composition of the stored hydrazine. The measured density and viscosity of stored hydrazine were both slightly lower than values used in calculations by JPL for hydrazine/water mixtures of the measured composition.⁴ For stock hydrazine, the density value reported was essentially the same as JPL used, but viscosity was about 3.5% lower than JPL's value. All differences noted were, however, insignificantly small for practical purposes (e.g., calibrating flow systems).

After being drained, the tank was purged with warm nitrogen to dry it out. Several weeks later it was flushed

³Dynamic Science Corporation, Monrovia, California.

⁴Values used in JPL calculations based on very careful measurements of physical properties made by Analytical Chemistry Section, JPL.

with a small amount of water and cut open for inspection. Many areas on the internal surface appeared to be discolored. In a random manner, the colors of the splotches were almost white, yellow-gray, blue-gray, and green-gray. In general, the dominant markings appeared as if a semi-liquid material had oozed out of the tank wall and drained downward toward the bottom of the tank. There were also some diffused circular rings, faintly resembling water level marks around a lake; these were probably related zones of variations in the metal surface, or a structural condition caused by the fabrication process. Since the inside of the tank was not seen until several weeks after having been drained, it is not known for certain what changes in the surface

took place between the time it was drained and when cut open. Figures 13 and 14, although lacking color definition, convey a good impression of the appearance of lower and mid-section parts of the surface at the time it was first inspected.

Samples for metallographic analysis were taken from a number of areas. Some were selected as being typical of the badly discolored or obviously pitted spots (samples 1 to 5), while others (samples 6, 7, and 8) were chosen, for purposes of comparison, from adjacent but "cleaner-looking" areas. The microstructures of these eight samples, after having been metallographically polished and etched, revealed some evidence of possible

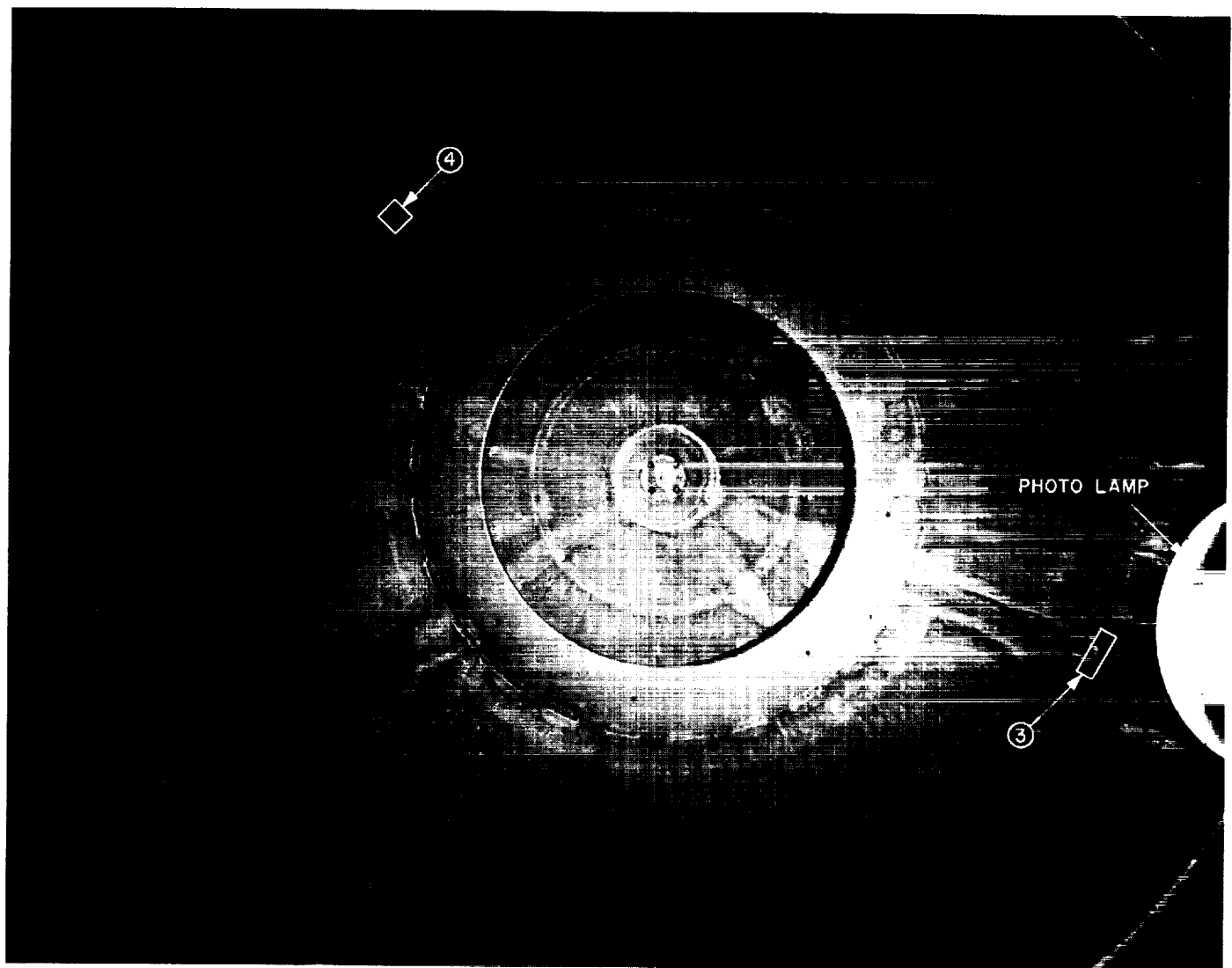


Fig. 13. Interior lower surface of Vega fuel tank after long-term hydrazine storage test and locations where metallographic samples No. 3 and No. 4 were taken

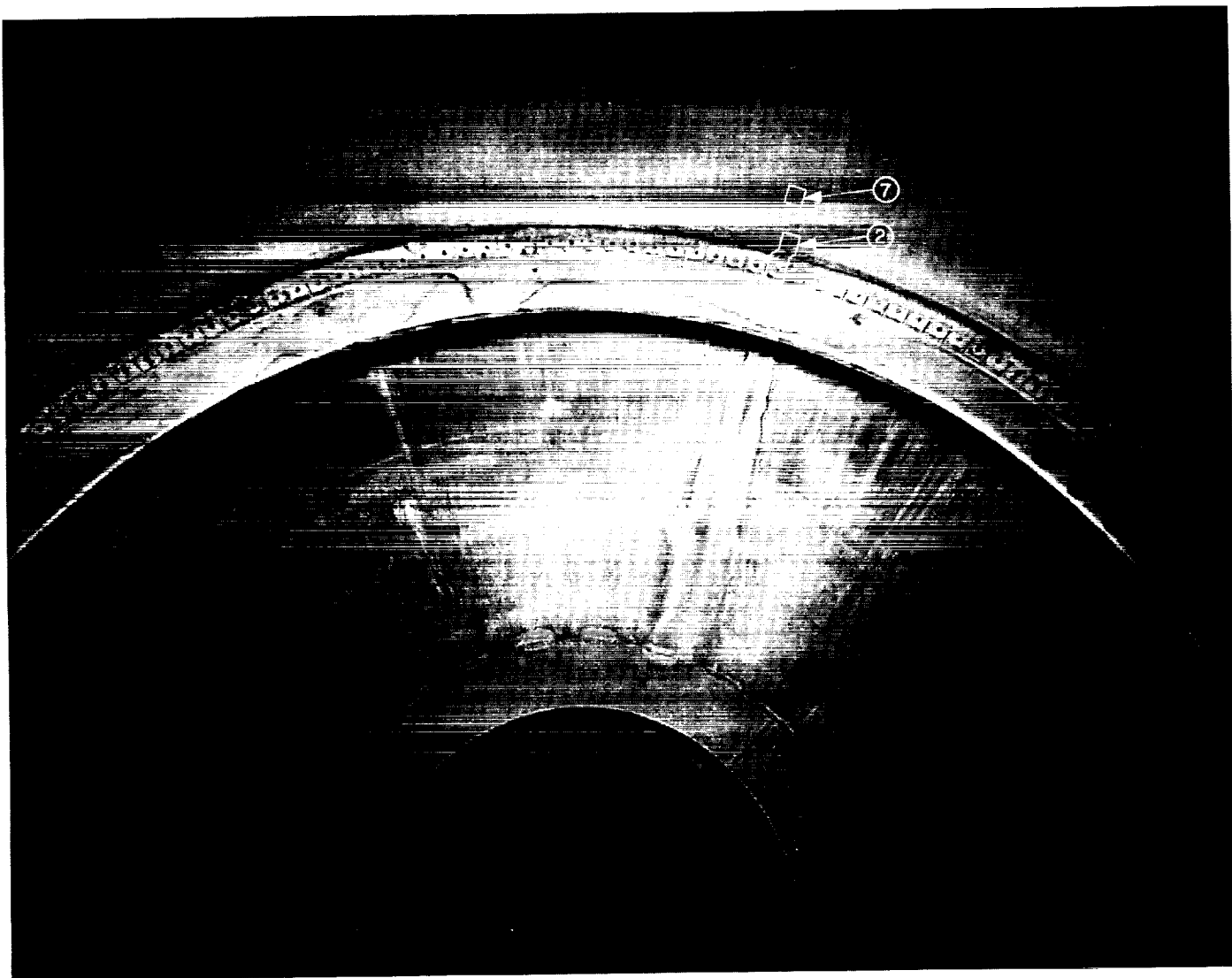


Fig. 14. Interior mid-section surface of Vega fuel tank after long-term hydrazine storage test and locations where metallographic samples No. 2 and No. 7 were taken

intergranular corrosion. However, in no case was the depth of pits found to be greater than 0.002 inch (Table 1). Figures 15 through 20 illustrate the most severe damage found in each specimen; two examples of exterior surface condition are shown for comparison.

The degree of corrosion seemed to vary considerably from area to area; the severest attack was limited to discrete spots, rather than covering extensive areas. Generally, discoloration was not indicative of the severity of corrosion, but corrosion was more prevalent in discolored areas than in the more normally colored areas. The cause of the discoloration was not determined. Although the exact corrosion mechanism was not established, the detection of copper and aluminum in the first few samples

Table 1. Depth of corrosion in Vega fuel tank specimens

Sample	Maximum depth of corrosion, mils
1	negligible
3	less than 1
4A	less than 1.7
4B	less than 1.5
5	negligible
6	less than 0.5
7	less than 1
8	less than 0.5



Fig. 15. Corrosion in Vega fuel tank specimen No. 4A, magnification $\times 500$

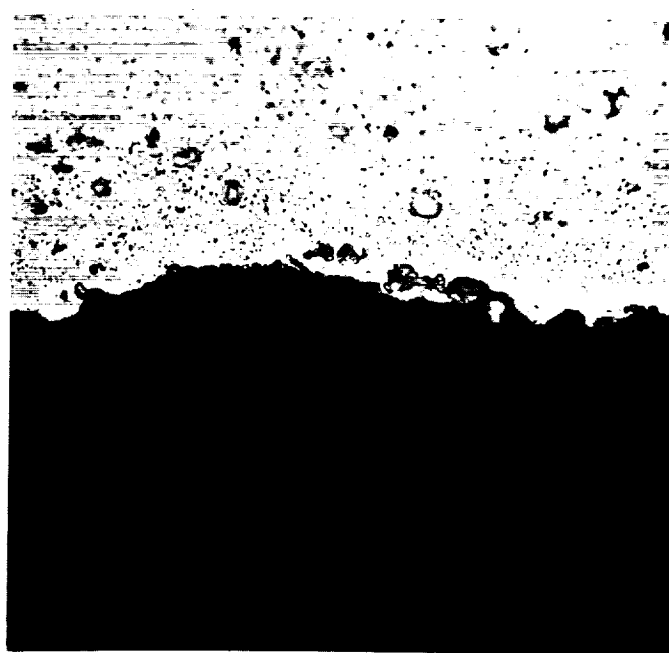


Fig. 17. Corrosion in Vega fuel tank specimen No. 6, magnification $\times 500$



Fig. 16. Corrosion in Vega fuel tank specimen No. 4B, magnification $\times 500$



Fig. 18. Condition of outside surface of Vega fuel tank specimen No. 9, magnification $\times 500$

of hydrazine taken from the tank might indicate the attack was, at least partially, a chemical dissolution (as contrasted with a possible alternate mechanism involving an electrochemical process). Lack of a further increase in the copper and aluminum content would then

have meant that all the observed degradation had taken place within the first few weeks of the exposure test. That finding would be in concert with those of the canister tests, where similar discoloration occurred within short periods.



Fig. 19. Corrosion in Vega fuel tank specimen No. 7, magnification $\times 500$

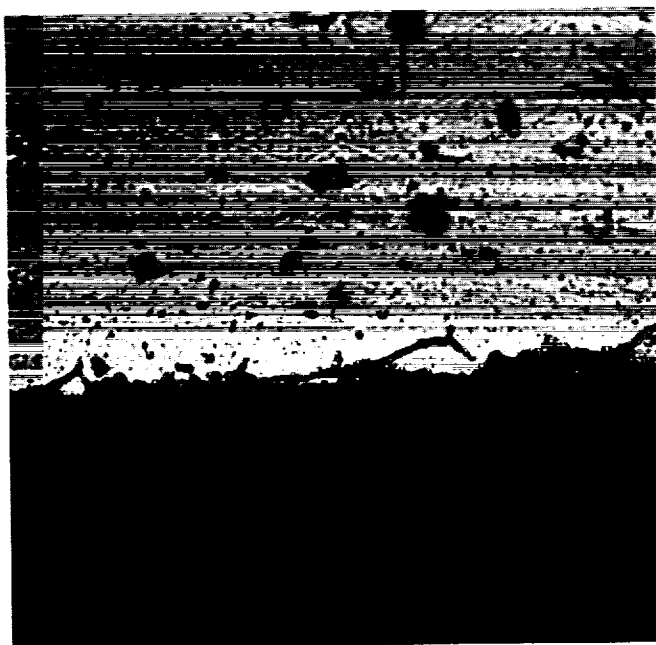


Fig. 20. Condition of outside surface of Vega fuel tank specimen No. 7, magnification $\times 500$

Each of the samples was also checked for hardness. The hardness survey was made on a Leitz Miniload tester, using the 100-gram Knoop indenter. Results are given in Table 2, along with conversions to equivalent

Table 2. Hardness test results from Vega fuel tank specimens

Sample	Knoop scale, 0.1 kg	Diamond pyramid ^a scale, 10 kg	Rockwell B ^b scale
1	144	128	71
2	106	102	57
3	161	142	77
4A	169	148	79
4B	162	142	77
5	159	140	76
6	154	137	75
7	147	132	73
8	154	137	75
2014-T4 ^b	124–148	116–132	65–73
2014-T6 ^b	172–200	150–169	80–86

^aConverted from Knoop scale.
^bComparison data from: "Metals Handbook," American Society of Metals, 8th Edition, 1961.

10-kilogram diamond pyramid hardness numbers and Rockwell B hardness numbers. The values range from 71 to 79 on the Rockwell B scale, except for sample No. 2 which was much softer (57 on Rockwell B). Sample No. 2 was taken from the area where one of the anti-slosh rings was welded to the tank, and it is possible that the softness in that area was caused by overheating during the welding process. The literature shows values of Rockwell B hardness ranging from 65 to 73 for type 2014-T4 aluminum alloy, and 80 to 86 for the same alloy in the T6 condition.

Four tensile test specimens were taken from locations near the top end of the tank and subjected to yield strength and ultimate tensile strength tests on a Baldwin-Lima Hamilton Mark G press. Data from such tests indicated the material of the tank was slightly less strong than the strength reported in the literature for new 2014-T6 aluminum alloy, but stronger than reported for 2014-T4. Table 3 presents a summary of the data

Based on the hardness and strength data, it was hypothesized that the tank was not originally in the T6 condition, as had been supposed, but was solution-treated and then allowed to age-harden at room temperature to the T4 condition. From results of the metallographic examination, it was concluded that corrosion was minimal and not detrimental to the strength of the tank.

Table 3. Tensile test results from Vega fuel tank specimens^a

Sample	0.2% yield strength, psi	Ultimate tensile strength, psi	Ultimate elongation, %	Young's modulus, psi
A	56,400	64,100	11	10,600,000
B	59,200	65,800	11	11,100,000
C	58,300	64,600	11	11,100,000
D	58,300	65,000	11	11,100,000

^aTests were made on samples of 0.036-square-inch cross-section at +75°F.

VII. Firing Tests of Stored Hydrazine

After the long-term storage test of the Vega fuel tank was completed, the hydrazine was drained into seven carefully cleaned hydrazine storage drums. The initial and final few pounds of liquid to flow out of the tank were combined in one drum. That sample—assumed to be the hydrazine which contained the most foreign material—and a sample of stock hydrazine were then subjected to several tests to compare their ignition and combustion characteristics. (The chemical compositions of these two samples of hydrazine were given in Section V.)

Five ignition lag tests (using apparatus described in Ref. 3) were performed with stock hydrazine and five

with the stored hydrazine. The lags measured in four tests with the stock hydrazine were 0.82 ± 0.08 milliseconds, which was approximately $\frac{1}{4}$ the lag previously measured for nearly pure hydrazine. The other test gave a value of 1.35 milliseconds. Lags with the stored hydrazine were 1.33 ± 0.18 milliseconds in four of the five tests; the remaining test showed a lag of 1.85 milliseconds. The data in Ref. 3 show that the addition of 1% water tends to reduce the lag; no data were obtained at higher water concentrations, so a direct correlation with lags reported here (for 1.28 and 1.86% water, respectively) was not possible.

In order to detect differences in performance and combustion smoothness between the stored and regular stock hydrazine when burned with N_2O_4 , a series of six rocket engine firing tests was made using the JPL MOD IV 100-pound thrust injector and a heavy, uncooled thrust chamber of 42 inches L^* . That injector was chosen for the tests because of its demonstrated reproducibility, from firing to firing; some data on this injector are given in Ref. 4. Figure 21 shows a cross-section view of the test engine assembly. The firing tests were made at JPL's Edwards Test Station with the engine installed (Fig. 22). To maximize the validity of the comparison, no changes in hardware were made during the series of six firings.

Thrust was measured by solid-state, crystal-type (Schaevitz-Bytrex Corporation, Waltham, Massachusetts) electronic load cells. Chamber pressure was measured by

Table 4. Summary of firing test data

Test No.	Fuel	Average effective (plenum) chamber pressure, P_c (psia)	Average mixture ratio, r (O/F)	Average oxidizer temp. T_o , °F	Average fuel temp. T_f , °F	Characteristic velocity, c^* , ft/sec				Specific impulse, I_s , lb _f -sec/lb _m			
						at 1 sec	at 2 sec	at 3 sec	at 4 sec	at 1 sec	at 2 sec	at 3 sec	at 4 sec
1	stock	147	1.17	88	90	5514	5512	5502	5502	N.C. ^a	216	216	216
2	stock	148	1.17	88	87	5505	5505	5484	5494	N.C. ^a	214	214	214
3	stock	149	1.17	87	87	5502	5541	5484	5498	N.C. ^a	213	211	211
4	stored	145	1.17	77	78	5413	5427	5392	5410	209	209	209	211
5	stored	148	1.18	77	77	5429	5433	5408	5436	205	210	207	209
6	stored	148	1.18	76	77	5432	5446	5408	5433	208	209	208	209

^aNot calculated because of thrust record inadequacies (undamped oscillations in thrust mount).

Note: All c^* calculations based on "cold" throat area. Four digits are shown for data consistency reasons only, not to imply four-place accuracy of the data.

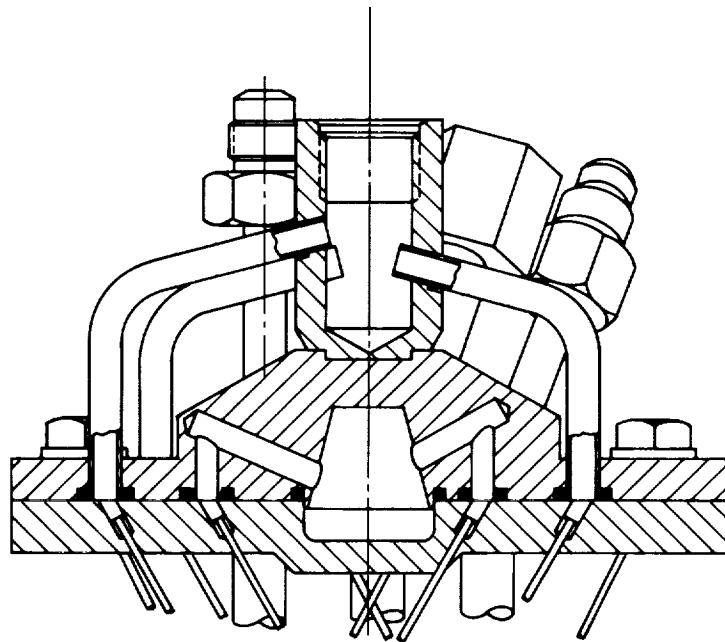
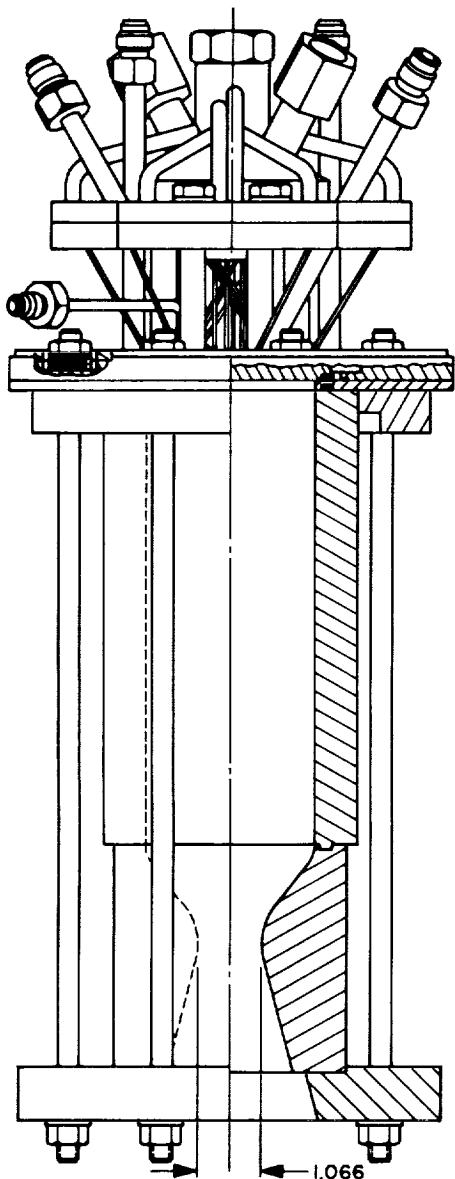


Fig. 21. Design of uncooled test rocket engine used to make comparison firings with stored and stock hydrazine fuel

Taber and flush-mounted Photocon pressure transducers. Fischer-Porter turbine-type flow meters were used to gauge the fuel and oxidizer flow rates. Before and after each test, the diameter of nozzle throat of the engine was measured with an internal micrometer at several places and the average was used to calculate the throat area.

Each test was approximately $4\frac{1}{2}$ seconds in duration, at a nominal chamber pressure of 148 psia and a nominal mixture ratio of 1.17. The first three tests were made with the stock hydrazine to establish a "standard" for

comparison. Then, three tests were made with the stored hydrazine. The average characteristic velocity, c^* , delivered with the stock propellant was 5500 ft/sec and the specific impulse, I_s , was 214 lb_f-sec/lb_m. A c^* of approximately 5420 ft/sec and an I_s of 208 lb_f-sec/lb_m were obtained with the stored hydrazine. Table 4 is a summary of the test data.

VIII. Summary and Conclusions

Ignition and steady-state operation appeared to be equally smooth with both stored and stock hydrazine.

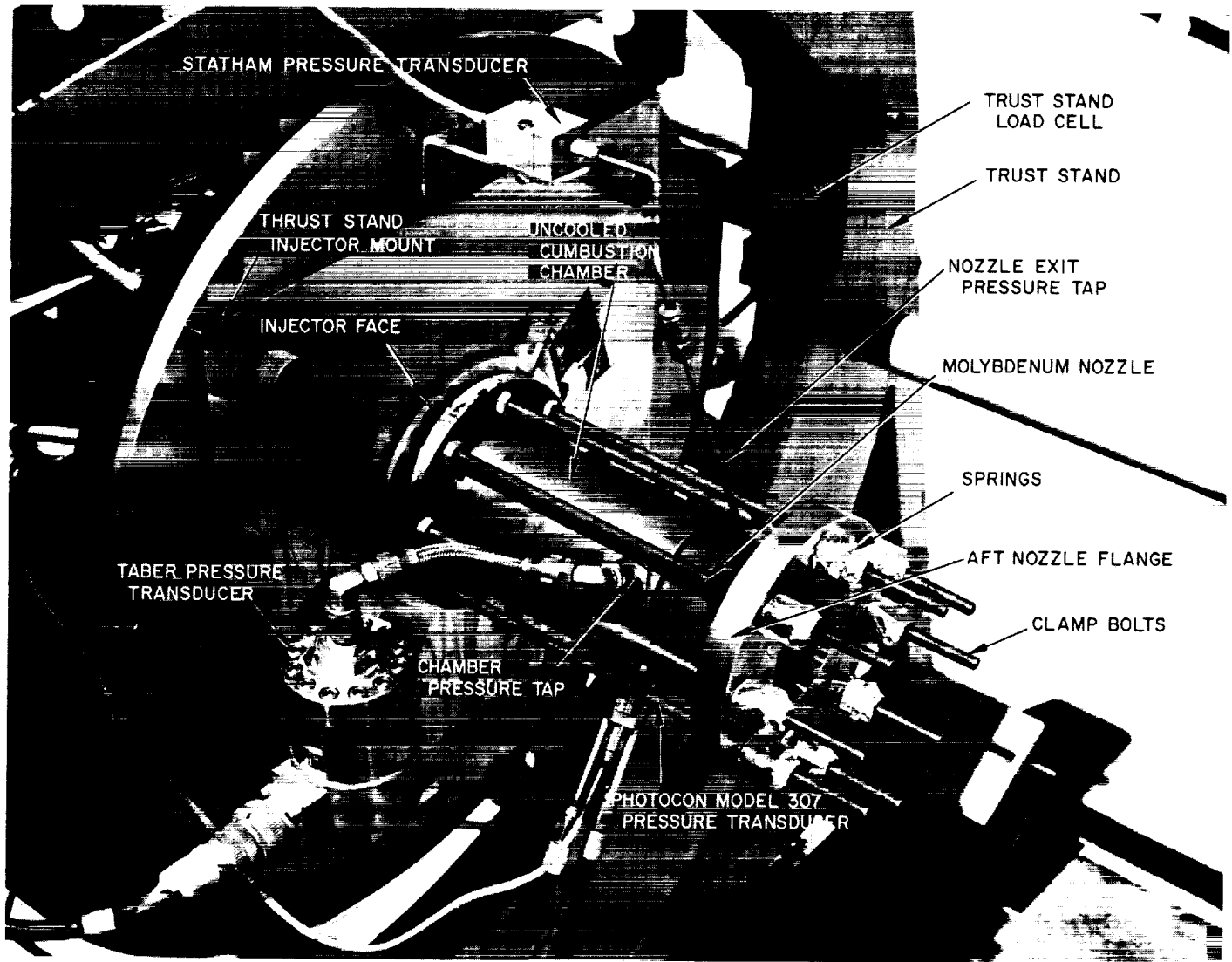


Fig. 22. Uncooled rocket engine on test stand at JPL's Edwards Test Station

As usual, the injector provided very smooth combustion; maximum peak-to-peak chamber pressure variations (random in form) were ± 2 psi, as measured by a flush-mounted Photocon pressure transducer located near the entrance to the converging section of the nozzle.

The difference in performance, as measured by characteristic velocity c^* or specific impulse I_s , was greater than anticipated based on the differences in chemical composition alone (presuming analytical results are representative of fuel as burned). That difference was not fully explained. Both theoretical shifting and theoretical frozen equilibrium performances were computed for various fuel mixtures and test conditions, using a JPL version of a performance program obtained from NASA's

Lewis Research Center. The program compared test results with theoretical loss in performance to be expected with increasing amounts of water and ammonia in the fuel; the changes in theoretical shifting equilibrium c^* with added ammonia and water are shown as plots in Figs. 23 and 24. The plots show that water added to pure hydrazine causes a drop of 15 ft/sec in c^* for each percent (by weight) of water in the resulting solution. Based on that figure, the difference in measured water concentrations would cause the stored fuel to deliver 9 ft/sec less c^* than stock fuel. Dissolving ammonia into the fuel has a lesser effect, since ammonia is a good fuel itself; each percent (by weight) of ammonia in the chosen base fuel (hydrazine with 1% water and $\frac{1}{2}\%$ aniline) lowers the c^* by only about 3 ft/sec.

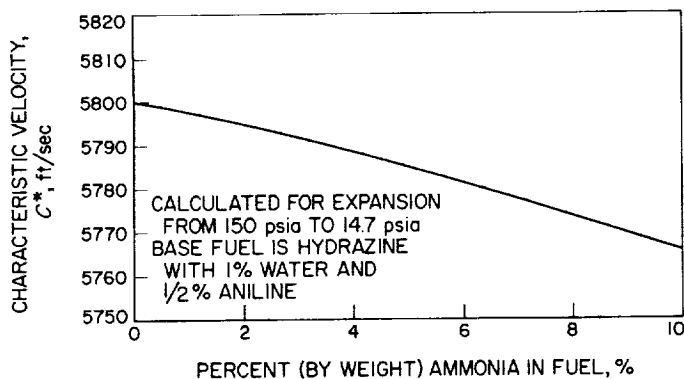


Fig. 23. Variation in theoretical shifting equilibrium c^* with addition of ammonia to hydrazine-base fuel burned with N_2O_4 at $r = 1.2$

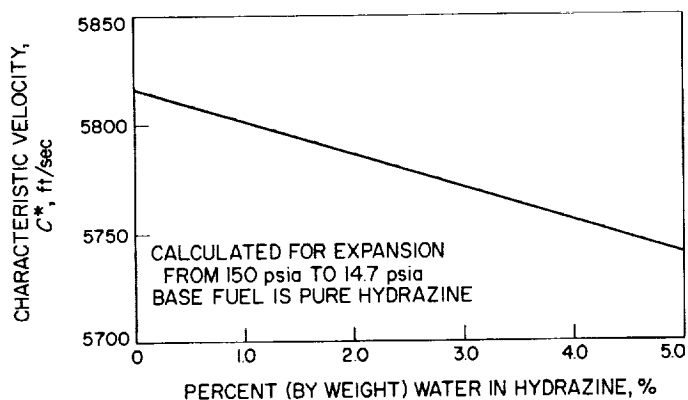


Fig. 24. Variation in theoretical shifting equilibrium c^* with addition of water to hydrazine when burned with N_2O_4 at $r = 1.2$

Obviously, the unaccounted for difference of 70 ft/sec could be explained on the basis of dissolved ammonia (evolved from decomposition of the hydrazine during storage) but the amount necessary would be improbably high.

Still, other possibilities did exist—such as the effect of dissolved nitrogen gas (the other decomposition product of hydrazine); this explanation would also be unlikely, since the change in the energy release caused by inert

gas is negligible, unless very great amounts are involved. More likely than affecting the true available energy per unit weight, dissolved gases (either ammonia or nitrogen) would cause effervescence in the fuel in lower pressure sections of the flow system. Thus, errors in flow measurement (due to unpredictable density) and disintegration of the liquid jets issuing from injector orifices would occur. The latter problem should have been minimized in the test injector because of the very short free-stream lengths; the former should have been minimized due to the very high drop across the injector orifices that resulted in high feed pressures in the upstream circuit where the flows were measured. Nevertheless, one or both of these two possible causes were judged to be the most probable reason for performance differences measured.

Some of the apparent performance difference may have been due to scatter, or errors in the measurements or data reduction, but this was not likely the entire cause, since the data displayed good consistency. For these tests, the maximum deviation in c^* , measured at any given time from start (i.e., at like throat temperature conditions), was only ± 18 ft/sec. If one point was rejected, the data would be consistent within ± 10 ft/sec. Specific impulse figures were consistent within ± 3 seconds. Flow rates were calculated based on counting individual cycles (to the nearest $\frac{1}{2}$ cycle) on the oscillograph traces. Pressure data were very carefully read from both oscillograph and strip chart records; all chamber pressure readings from the oscillograph agreed within 0.5 psi with data taken independently from strip chart records. While test-to-test consistency was an indication rather than a proof of accuracy, it was judged that errors arising from data measurement (excepting flow rates, for the reason stated above) and data reduction were minimal.

The conclusion reached at this writing is that the most degraded hydrazine taken from the storage test had properties which were slightly different from the stock propellant, but still suitable for firing, provided the possibility of a slight lowering of performance would not be detrimental. No seriously adverse effects were observed.

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Appendix

Table A-1. Cleaning specification

Solution	Purpose	Formula	Temp, °F	Time, min	Control
a.	Cleaning	Liquid detergent ½-1 oz per gallon	180	As required	50 ppm of particulate matter with maximum size of 10 microns: pH 6.5-7.5
b.	Distilled water rinse		120	As required	pH 6.5-7.5
c.	Pickling (aluminum)	Chromic acid, 80 lbs; phosphoric acid, 20 gal; nitric acid, 15 gal (per 100 gal solution)	Room	As required	15 grams aluminum per liter solution
d.	Distilled water rinse		120	As required	pH 6.5-7.5
e.	Passivating (aluminum)	Chromic acid 11%	Room	5-10	10 grams aluminum per liter of solution
f.	Distilled water rinse		120	As required	pH 6.5-7.5
g.	Passivating (hydrazine service)	Hydrazine 10-25% by volume with distilled water	Room	24 hours	none (solution not reusable)
h.	Neutralizing	Turco No. 4215, 2 oz per gallon of water	Room	5	pH greater than 7.5

